Recent Progress in NIF Mandrel Production

M. Takagi, R. Cook, B. McQuillan, A. Nikroo

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Masaru Takagi, Robert Cook, Barry McQuillan, Abbas Nikroo

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550
email: takagi@gat.com
Fusion Group, General Atomics, P.O. Box 85608, San Diego, California 92186-5608

The production of spherical poly(α-methylstyrene) (PαMS) mandrels utilizes a small amount (<0.1wt%) of high-molecular-weight poly(acrylic acid) (PAA) in the suspending medium, which substantially increases the interfacial tension during curing relative to methods using poly(vinyl alcohol) (PVA). However, fully cured capsules made by this method displayed a significant level of high frequency surface debris that became especially problematic when the mandrels were subsequently overcoated. To solve this problem we examined the use of PAA in conjunction with PVA in order to reduce these surface features, and explored numerous variations of concentration and timing of the PVA addition. The optimum conditions were found to be initial use of PAA for centering and symmetry of the mandrels, followed by removal of the PAA medium, washing of the mandrels with water, and finally transfer to PVA solution for completion of the curing cycle

I. INTRODUCTION

The basic microencapsulation process used in producing PαMS mandrels involves using a droplet generator to produce a water droplet (W1) encapsulated by a fluorobenzene solution of PαMS (O), this compound droplet being suspended in a stirred aqueous bath (W2). Historically this bath has contained poly(vinyl alcohol) (PVA, 88% hydrolyzed, mol. wt. ~25,000 g/mol) to prevent agglomeration of the initially fluid compound droplets. Replacement of the PVA with poly(acrylic acid) (PAA, mol.wt. ~10^6 g/mol, W2=0.05 wt% PAA) resulted in a major improvement in sphericity due to a greatly increased interfacial tension between the bath and the compound droplet, relative to the use of PVA as the bath additive.[1] PαMS mandrels produced using PAA in the bath along with slow curing to suppress Marangoni convection that was

perturbing the mode 10 to 20 symmetry[2] resulted in 2 mm diameter PαMS shells with mode 2 out-of-round[3] (OOR) of ~0.5 μm (as well as non-concentricity[4] (NC) <1%) which meet the capsule design requirements. A representative set of equatorial traces produced by our AFM-based Spheremapper[5] along with the computed power spectrum is shown in Fig. 1 for an average shell. Although the power spectrum is at or below the design specification at nearly all modes one can see in the traces some degree of roughness which manifests itself at the very high modes in the power spectrum.

When these shells were overcoated with GDP prior to the pyrolysis step it was found that the resulting surface was covered with small domes. In Fig. 2 we show a SEM image of a shell surface with a 55 μm GDP coating, and below it a set of representative equatorial traces and the resulting shell power spectrum. Clearly the high frequency roughness on the PαMS shell has seeded defect growth[6] in the GDP layer, producing an unacceptable

This phenomenon does not occur when PVA is used in the bath, thus we concluded that the PAA was leaving a fine residue on the PαMS shell surface. The PAA aqueous bath solution may contain minute gel particles that are not captured by the 3 μm pore size filter used in preparing the solution. Attempts to remove the gel with finer pore size filters were unsuccessful, resulting in vanishingly small filtration rates or simple clogging. We believe that the residue on the PαMS shell surface was PAA which adsorbed onto, or became embedded in the surface during curing.

We will describe the techniques that were developed to remove the adsorbed material from the PαMS shells. A key consideration in the development of the techniques used was the necessity of not simultaneously degrading the greatly improved sphericity the PAA provides.
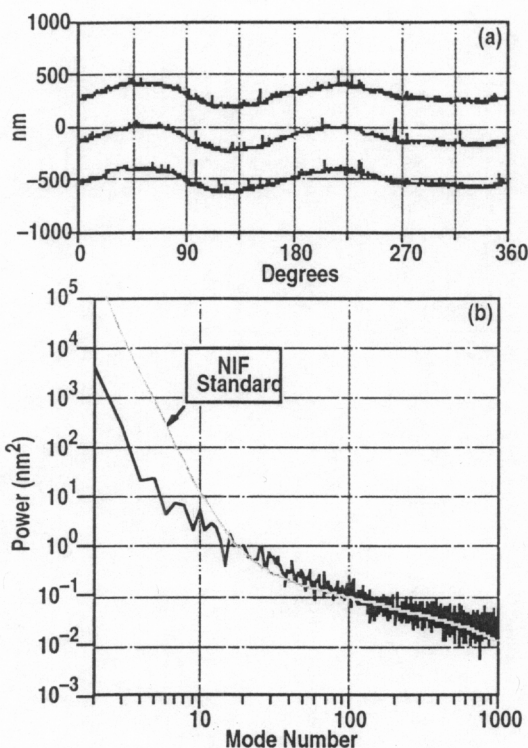
Fig. 1. Representative equatorial traces and the power spectrum from an average shell produced in PAA.

II. INVESTIGATION OF METHODS TO REMOVE PAA FROM THE SHELL SURFACE

II.A. Washing

Our first approach was to enhance the washing process of the fully cured shells. Typically the process involves several rinses with water. However we felt that we could take advantage of the carboxylic functionality of the PAA by washing with basic and acidic media. We subjected a set of shells to a wash cycle consisting of first pure water, followed by dilute NaOH, pure water, dilute HCl, and finally pure water again. There is some significant improvement. Attempts to improve the process by adding additional wash cycles did not lead to further improvement and thus we proceeded to explore the options below.

IIB. PVA/PAA Combination Process

We next turned to the use of PVA as an agent that might remove PAA or prevent it from depositing. PVA alone, even at much higher concentrations than those used for PAA, rinsed completely off leaving no deposits. Our first approach was to produce the W1/O compound droplet shell precursors using PVA in the W2 phase, and then replaced varying fractions of the PVA solution with PAA solution before completing the cure at 25°C. In this way we hoped to keep the oil surface covered with a PVA layer while the interfacial tension might be enhanced by the
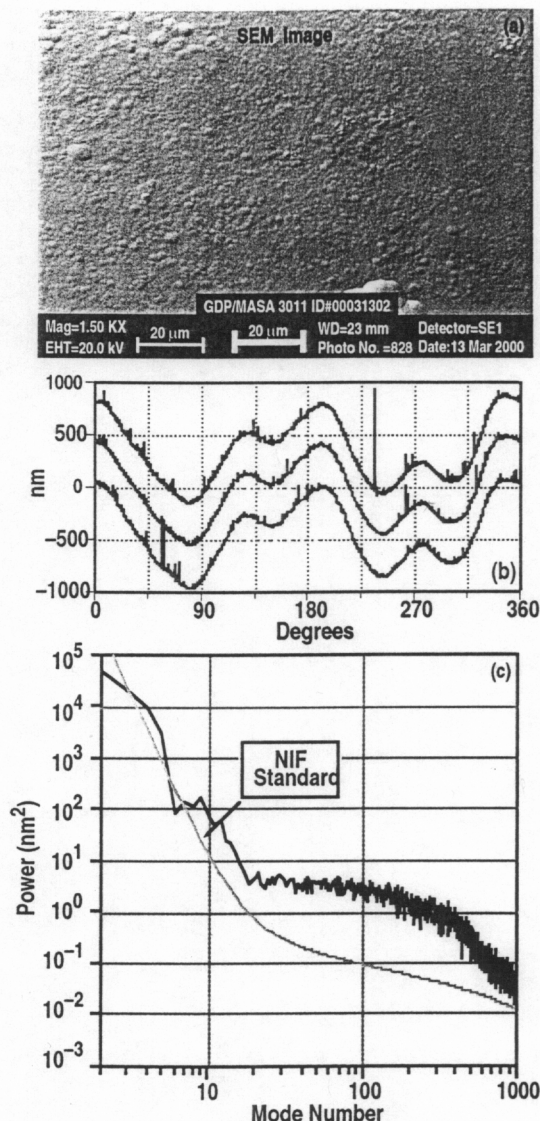

Fig. 2. At the top is an SEM image of a 55 μm coating of GDP on top of a PAA prepared shell. Below are representative equatorial traces that show numerous "spikes" due to dome formation. At the bottom is the shell power spectrum which shows significantly enhanced power at the mid to high modes.

PAA. A number of PVA:PAA final concentration ratios were examined (Table I). The OOR increased above the NIF spec of 1.0 μm. This increase is not surprising since if the PVA was in fact coating the oil phase surface with a lower interfacial tension, a higher OOR is anticipated. In addition, there is still visible debris manifest in the form of small spikes on the equatorial traces.

II.C. PAA/PVA Combination Process

In this process, we attempted to set the shell sphericity with a PAA bath before adding PVA. Specifically W1/O

Table I. Conditions tested using the PVA/PAA
combination process and the average OOR and NC

Ratio		Trials	OOR μm	NC %
PVA:	PAA			
0.16% :	0.042%	2	3.9	1.8
0.25% :	0.038%	7	1.1	<1
0.33% :	0.033%	2	1.0	<1
0.50% :	0.025%	2	1.2	2.4

viscosity of the oil phase to increase and set the low mode geometry of the shell,[7] and then PVA was added to the compound droplets were prepared in a 0.05% PAA bath and were cured in this bath for a period of time to allow thebath in increments as shown in Table II. A detailed example of the process (sixth line of Table II) is formation and partial curing in 240 ml PAA, addition of 10 ml 10% PVA after 23 h resulting in a net 0.4% PVA concentration in the bath, followed by addition of an additional 50 ml of 10% PVA after the 42 h resulting in a 2 wt% PVA concentration in the bath.

The shell OOR was sensitive to the time of the first addition, short times resulting in greater OOR's as expected. In general, however, the approach was very effective in both maintaining shell sphericity and improving the surface finish of the shells. Representative equatorial traces and a power spectrum for the example condition detailed above are shown in Fig. 3. There was some difficulty with reproducibility, in part because the cure time for each batch depends to some extent on the number of shells produced.

II.D. PVA Exchange Method

Noting our success in adding PVA to the PAA bath to displace residue from the surfaces and our success in preserving the basic shell symmetry by waiting until the oil phase viscosity had increased sufficiently, our next approach was to replace all of the PAA with high concentration PVA after an initial curing period. For example (first line in Table III) the compound droplets are cured for 27 h in 0.05 wt% PAA and then the PAA is decanted off, the shells rinsed gently with water, and then 3 wt% PVA is added as the bath fluid and the curing continued in the rotary bath for an additional 2 days.

Representative traces and the power spectrum for a typical shell prepared by this method are displayed in Fig. 4. The resulting shells are both spherical and reasonably free of surface debris. As a confirmatory test we show in Fig. 5 a surface patch SEM image (compare with Fig. 2) along with representative equatorial traces and the power spectrum of a typical PVA exchange process shell that has been overcoated with 14 μm of GDP and then pyrolyzed to produce a GDP shell.
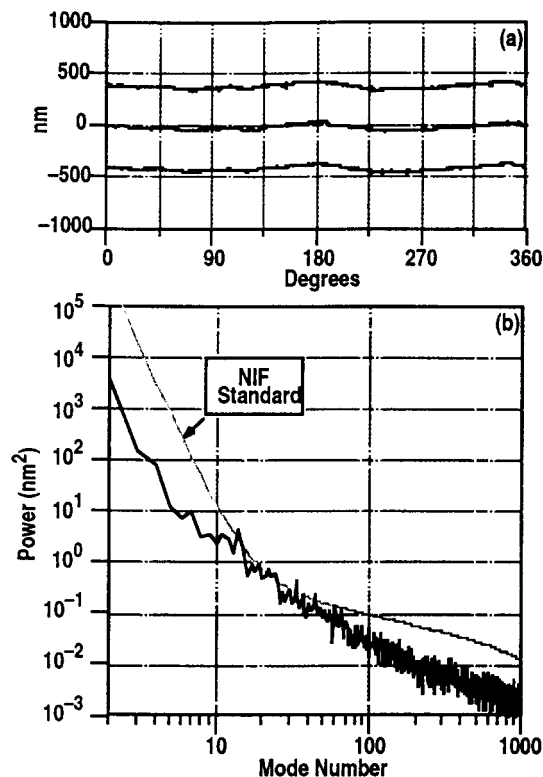

Fig. 3. Representative traces and power spectrum of a shell prepared by the PAA/PVA combination method.

Table II. Conditions tested using the PAA/PVA
combination process. All NC were less than 1%

Time (h) of PVA addition and resultant wt% PVA

1st	PVA %	2nd	PVA %	3rd	PVA %	Trials	OOR μm
4	0.3	24	0.7	48	1.3	2	2.3
6	0.3	24	0.7	48	1.3	2	1.0
7	0.3	24	0.7	48	1.3	2	1.0
26-28	0.3	45-47	1.0	53	2.0	4	1.1
10-14	0.3	22-26	2.0	—	—	6	0.9
22-25	0.3	42-48	2.0	—	—	12	0.8
29-31	0.5	45-48	0.9	—	—	6	1.1
41-43	0.3	65-67	2.0	—	—	4	0.7
17-19	2.0	—	—	—	—	4	0.6
22	2.0	—	—	—	—	2	1.0
23	2.0	54	3.0*	—	—	2	0.9

* all PAA removed prior to addition of 3% PVA

Table III. Conditions tested using the PVA exchange
process and the resultant average OOR and NC

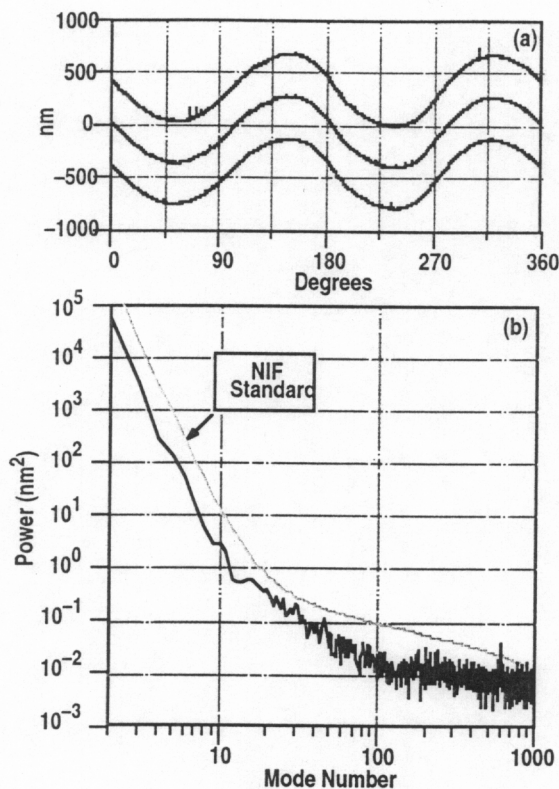| Cure Times		Trials	OOR μm	NC %
PAA (h)	PVA (h)			
25-27	51	4	0.7	<1
28-30	48	8	0.6	<1

Fig. 4. Representative traces and a power spectrum of a shell prepared by the PVA exchange method.

III. REPRODUCIBILITY

We investigated exchanging PAA with three different types of PVA: PVA 25 K MW, 88% hydrolysis; 25 K MW 98% hydrolysis; and 125K MW, 88% hydrolysis. 2-3 wt% PVA solution is exchanged with an initial 0.05 wt% PAA solution. The exchanges are done after 48 h of curing, when the shells are nearly cured. The PAA to PVA molecular ratio is 1 to 6120–9187, so we can assume the PVA floods the shells surface, removing the PAA.

Figure 6 shows the AFM power spectrum of a random sampling of ten shells in the same batch (#6014) that were made by decanting PAA after 48 h, rinsing with water and exchanging with 2 wt% 25 K PVA (98% hydrolysis), then returning to finish the curing. Almost all shells' power spectra fall below the NIF standard power specification curve. One shell had problem across the high modes, caused by one or two spikes.

Figures 7 and 8 show the reproducibility of twenty runs (PαMS and GDP coated shells) using 2% 125 K PVA (88%) for the exchange. We made the initial shells using W2 = 0.05 wt% PAA, and started curing at 25°C. We then changed to 2% 125 K PVA (88%) after 48 h, and restarted the curing at 50°C for another 48 h. The Fig. 8 GDP coated shell shows a middle mode and high mode problem in one trace. The middle mode problem is caused by a localized
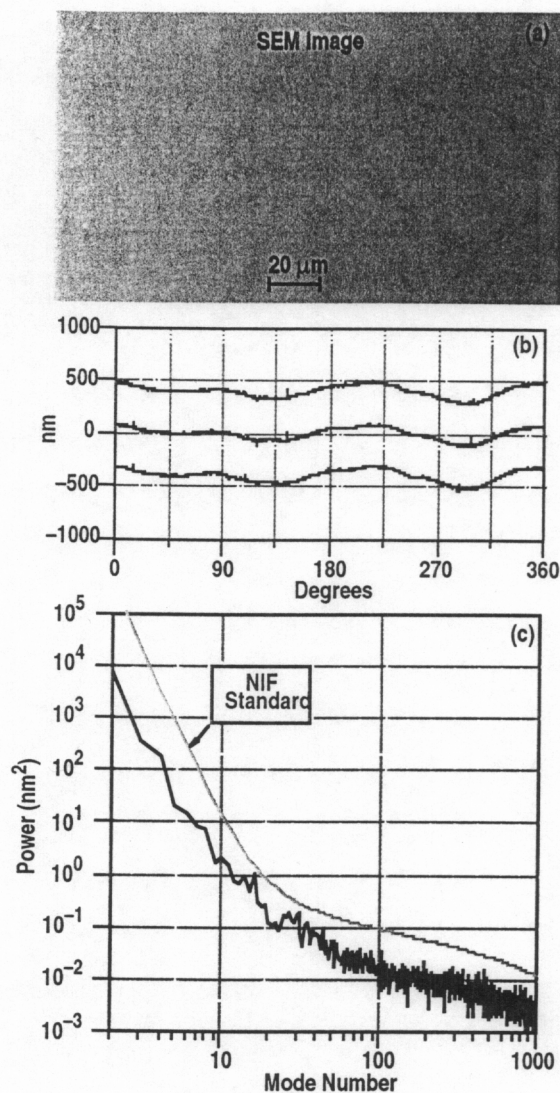

Fig. 5. At the top is an SEM image of a GDP shell prepared from the PVA exchange method PaMS mandrel. Below are representative equatorial traces and the power spectrum.

implosion created in the water/alcohol W1 extraction process. The high mode portion is caused by one to two spikes. Figure 7 shows 40% yield of NIF quality PαMS mandrels. The yield of NIF quality mandrels is higher using the high molecular weight PVA than low molecular weight PVA or high hydrolysis PVA.

IV. DISCUSSION AND SUMMARY

We have shown that PVA is effective at removing adsorbed PAA from the surfaces of PαMS shells. Further the fundamental shell symmetry, primarily the mode 2 OOR and NC, can be set by an initial formation and cure in

PAA until the oil phase is viscous enough to resist distortion, before exchanging with PVA.
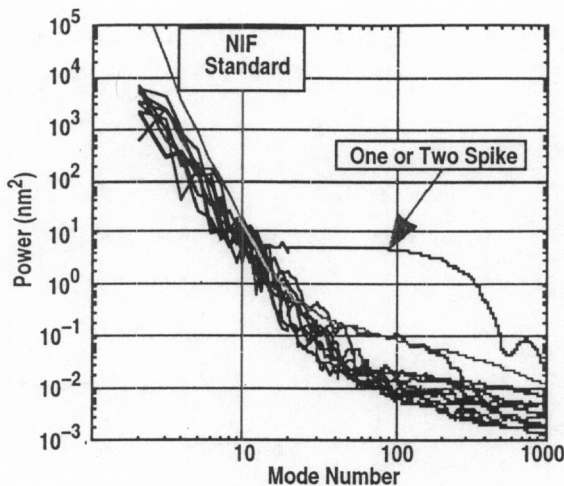
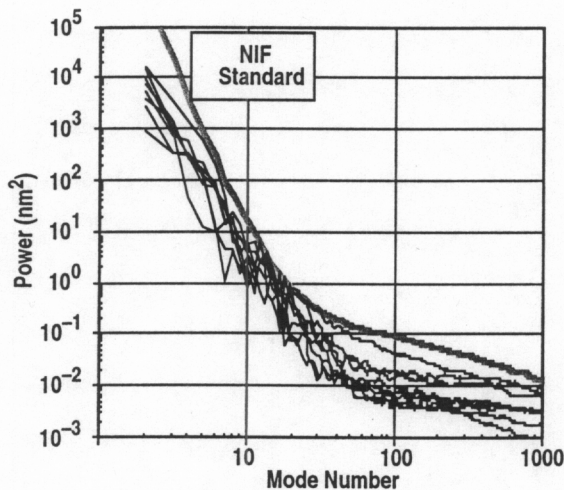Fig, 6 AFM power spectrum of a random sample of ten shells from batch #6014.

Fig. 7. AFM power spectrum of 40% good yield shells in 20 runs.

The production process for PαMS mandrels is improved by utilizing a PAA/PVA exchange process. Our best and most reproducible results come when the initial compound droplets cure and stiffen in a 0.05 wt% PAA rotary bath for about 24 h to set the overall sphericity, and then replace the PAA with 3 wt% PVA for an additional 2 days of treatment in the rotary bath. The advantages of PAA for low mode sphericity are maintained, and the resulting PαMS shells and GDP shells made from them meet or exceed the target surface design requirements at all modes.

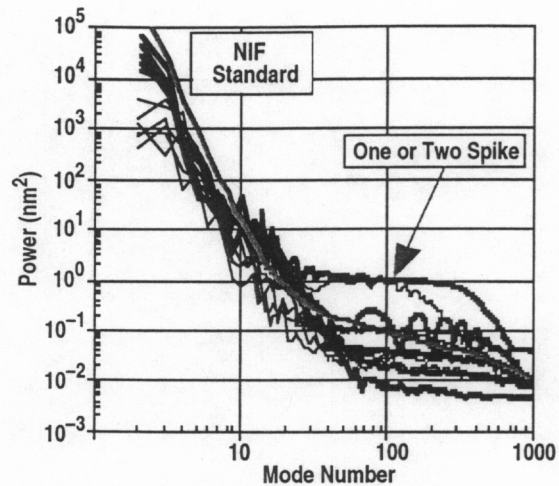Fig. 8. AFM power spectrum using same shells after GDP (thin line) coating and after pyrolysis PaMS (thick line) from batch #6014.

ACKNOWLEDGMENT

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2. B.W. MCQUILLAN and M. TAKAGI, "Removal of Mode 10 Surface Ripples in ICF PαMS Shells," *Fusion Technol.* this issue.
3. Out-of-round is defined as the difference between the maximum and minimum radius.
4. Non-concentricity is the offset of the center of the outside surface from the inside surface, normalized to the wall thickness; it must be less than 5% in the mandrel to achieve uniform walls in the shell formed on it.
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